

ART. VIII.—*The Spectra of the Alkalies and their Atomic Weights.*

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In a paper read before the Royal Society of Victoria in November last year, I introduced the formula $\lambda = x + \frac{y}{n^2 - z}$, by which to express the relationship of several spectrum lines of the same metal. The three constants x , y and z I determined from three successive wave lengths, n being assumed a round number and found experimentally. In order to test the validity of the last assumption and to effect a better accordance between the experimental and the calculated values, I have added a fourth wave length and determined the value of n by an additional equation. If a , b , c and d are the numbers representing the wave lengths of four successive spectrum lines of a series, their relations may be expressed as follows :

$$a = x + \frac{y}{n^2 - z}$$

$$b = x + \frac{y}{(n+1)^2 - z}$$

$$c = x + \frac{y}{(n+2)^2 - z}$$

$$d = x + \frac{y}{(n+3)^2 - z}$$

and their constants found by the four equations :

$$1. \quad x = a - \frac{y}{n^2 - z}$$

$$2. \quad y = \frac{(a-b)(n^2-z)[(n+1)^2-z]}{2n+1}$$

$$3. \quad z = n^2 - \frac{(b-c)(2n+1)(4n+4)}{(a-b)(4n+4) - (a-c)(2n+1)}$$

$$4. \quad n^2 + 3n = \frac{27a - 32\beta}{16\beta - 12a}$$

$$\text{if } a = a - c \text{ and } \beta = \frac{(a-d)(b-c)}{b-a}$$

The fourth equation, being quadratic, yields two values, the lesser one applying to the first and the larger one to the fourth member of the series.

The value of n may also be found by approximation, viz., by substituting successively probable values for n into equation No. 3, until the most satisfactory results are obtained. Both methods may be employed, the first when the experimental data are very correct, the latter in doubtful cases.

The values of n , x , y and z , determined from the experimental data for the alkalies and Helium, are contained in the table of spectral constants given below, from the study of which the following results have been derived.

Calling x the root and n the modulus, and denoting the principal series by a , a^1 and a^2 , the subordinate series by b , b^1 , b^2 and c , c^1 , c^2 , I have arrived at the propositions:—

1. Each element has two roots for its four subordinate series, and two, possibly only one, for its two head or principal series.

2. The modulus of the subordinate series b , b^1 , b^2 is a round number, of the coordinate series c , c^1 , c^2 a fractional value.

I propose to call the series b , b^1 , b^2 the normal, the series c , c^1 , c^2 the abnormal one.

3. The atomic weights are directly proportional to the square roots of the difference of the roots (x) of the subordinate series.

In the following little table the first line contains the difference of the roots of the subordinate series for each element; the second, the square roots of these numbers; the third, the atomic weights, and the fourth, the atomic weights divided by the square roots.

Helium.	Li.	Na.	K.	Rb.	Cs.
·10	—	4·0	11·53	54·86	134·7
·316	—	2·0	3·395	7·406	11·61
4?	7	23	39	85·2	133
12·65?	—	11·5	11·49	11·5	11·46

The constancy of the last line for the alkalies proves the proposition.

Whether the two head series start from a single root or not is a point I have, so far, not been able to settle. The data to hand are not sufficiently precise, or the series too short. The modulus advances in value with the atomic weight, viz., Helium = ·94;

Li = .96; Na = 1.2; K = 1.44; Rb = 1.57 and 1.61; Cs (probably) = 1.75.

Mr. William Sutherland, who most kindly volunteered to assist me in drawing up my report, and has also kept me informed of the latest intelligence bearing on this paper, has discovered the following remarkable relation, communicated to me in these words:—

“If you take your series of numbers
 .96 1.2 1.44 1.57 and 1.61 1.75
 and write their differences you get
 .24 .24 .13 or .17 .18 or .14
 while the differences of atomic weights are
 16 16 46 48

whose square roots are nearly inversely proportional to the previous numbers.”

My second proposition leads to a considerable simplification in the process of evolving the constants. After first having ascertained which of the series is the normal, *i.e.*, yields precise results with three constants only according to equation No. 3, the roots thus obtained lead to the determination of the moduli of the co-ordinated abnormal series. If a , b and c are three successive wave lengths with their roots subtracted, the modulus is found by the equation—

$$n = \frac{4\left(\frac{a}{b} - 1\right) - \left(\frac{a}{c} - 1\right)}{2\left(\frac{a}{c} - 1\right) - 4\left(\frac{a}{b} - 1\right)}$$

My constants have been obtained from three wave lengths only for the normal series, excepting the series b^1 of Sodium, where discrepancies exceeding the probable limit of error of observation induced me to harmonise my results by rejecting the third wave length and employing in its stead a mean value derived from the other members of the series.

For the ultrared rays of Lithium and Sodium I have adopted the very accurate numbers found by E. P. Lewis, in preference to those of Kaiser and Runge. Swan's numbers for the same part of the spectrum in regard to Potassium, Rubidium and Caesium can only be considered as widely approximative. The spectra of the two last named metals are, in my opinion, incomplete; Rubidium wanting another pair of abnormal series for

its completion, and Caesium a pair of normal series. This may account for some discrepancies in my table of wave lengths and likewise reinstate several wave lengths rejected in my first paper.

The atomic weights, taking Sodium = 23, may be calculated from proposition No. 3 as follows:—Helium = 3·64; Na = 23; K = 39·05; Rb = 85·15; Cs = 133·47. Kaiser and Runge calculated the atomic weights from the differences of the vibration numbers and obtained the values, viz., Na = 23; K = 40·6; Rb = 82·6; Cs = 126.

I may state here that the same proportionality prevails in the second group of elements, and even in the other groups, where series have been discovered. In the case of triplets the first and the third wave length yield the proportional value. My investigations on those groups have, however, not been concluded. I, therefore, refrain from giving the numbers.

Rydberg's proposed law connecting the roots of the subordinate series with the headlines and root of the principal series, although not strictly true for Helium and Potassium, I have made use of for the approximate determination of the modulus of the head series of Caesium.

T. Balmer has quite recently published a formula similar to mine with three constants. Its application to the Helium lines shows good accordance, excepting the c^1 and c^2 series, where it fails to the extent of more than 10 Angstroem units. His paper is published in Wiedemann's *Annalen der Physik und Chemie*. The same periodical is the source from whence the experimental data of my paper have been derived, except the Helium series, which have been published by Runge and Paschen in the *Sitzungsberichte der Academie in Berlin* last year.

In my table of wave lengths the experimental values and the calculated ones are placed one above the other, those on a line with E, E being the numbers derived from observations and corresponding to those immediately above.

If I may allow myself any conjectures regarding the nature of the curves and the origin of the spectrum lines, I consider the curves to belong to the conical order—hyperbolas in preference—while the lines are caused by the interference of two light waves, the distance of one line from the next following being consistently $2n + 1$.